J Mater Sci (2011) 46:1635–1639
DOI 10.1007/s10853-010-4979-1

Structural and electronic properties of 0.5 ML sulfur adsorbed on the GaP(001) surface

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Received: 22 June 2010 / Accepted: 4 October 2010 / Published online: 20 October 2010

Abstract The structural and electronic properties of 0.5 ML S adsorption on the Ga- and P-terminated GaP(001) (1 × 2) surfaces were studied by first-principles total-energy calculations. Sulfur adsorbates prefer to occupy the bridge sites on the Ga-terminated surface, consistent with the experimental results. Electronic analysis shows that the surface state around the Fermi energy (E_f) vanishes for S-adsorbed P-terminated surface at the substitution site. In the case of S-adsorbed Ga-terminated surface at the bridge site, the surface state at E_f is tremendously lowered but not completely diminish, which is in good agreement with the experiments. The S-induced work-function changes on the Ga- and P-terminated surfaces are 1.44 and 0.45 eV, respectively, indicating that some charge is transferred from the substrate to the S adsorbate. The Ga-S stretching vibrational frequency is calculated to be 37.61 meV.

Introduction

Most III–V compound semiconductor surfaces are characterized by a high density of surface states in the band gap, which results in rigid pinning of the Fermi level [1]. This has negative effect on the operation of many optoelectronic devices. To eliminate the undesirable effect on the surface, surface passivation is often taken into account.

The passivation effects of sulfur adsorption on GaP(001) surface have been studied by many experiments and it was confirmed that this effect can substantially decrease the density of states in the band gap and considerably slow down the oxidation of the GaP surface. Fukuda and collaborators [2–7] studied the structure of S adsorption on GaP(001) surface by means of low-energy electron diffraction (LEED), scanning tunnelling microscopy (STM), Auger electron spectroscopy (AES), inverse and ultraviolet photoemission spectroscopy (IPES and UPS), X-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS). The passivated surface was treated by different solutions of $(NH_2)_2CS$, $(NH_4)_2S_x$, $P_2S_5/(NH_4)_2S_x$, and $S_2Cl_2/(NH_4)_2S_x$ or the gas phase of hydrogen sulfide. The (1 × 2) structure was observed, for the first time, with H_2S treatment at 450 °C [2]. The coverage of sulfur was estimated to be half monolayer (ML) by AES measurement [3]. XPS and STM studies suggested that sulfur atoms only bonded to gallium atoms and occupied the bridge sites between the gallium dimers. Nevertheless, Yuan et al. [8] found that the stable P–S bonding was formed on the surface with the treatment of neutralized $(NH_4)_2S$ solution. With the $(NH_4)_2S_x$ treatment, the P–S bonding was also observed in spite of tremendous decrease in intensity upon annealing the surface at 400 °C [9]. Additionally, for the similar III–V compound passivated surface of InP(001) (1 × 2)-S, the analysis of low-energy electron diffraction showed that the most possible reconstruction is a mixed In-S dimer on the top surface [10]. Recently, 0.5 ML S adsorption on InP(001) surface was studied by Tian et al. [11] using density-functional total-energy minimization theoretical methods and core-level photoemission spectroscopy, and it was found that the most stable structure was a (2 × 2)

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reconstruction with rows of S–P and P–S pairs. Therefore, the surface structure and passivation mechanism still remain unclear. To the best of our knowledge, no calculations on the structural and electronic properties of 0.5 ML S adsorption on the GaP(001) surface have been reported so far. It is, hence, necessary to perform calculations for these properties using the density-functional theory (DFT) method within the generalized gradient approximation, which has proved to be useful in calculating both structural and electronic properties of medium-sized systems [12–15]. This study provides significant insight into understanding the character of chemical bonding between S and substrates and the electronic properties of the S-adsorbed GaP(001) (1 × 2) surface.

Calculation method

Our calculations were carried out within the DFT framework. The computer code used was VASP. The electron–ion interaction was described by projector augmented wave method (PAW) [16]. We employed the generalized gradient approximation (GGA) using the exchange-correlation functional according to Perdew and Wang [17, 18]. The electronic ground state was calculated with the residuum-minimization techniques. The geometric structure was optimized with the conjugated-gradient technique. The wave functions have been expanded in plane waves with a cutoff energy of 450 eV. Integration over an irreducible Brillouin zone was carried out using the Monkhorst–Pack grid of 6 × 6 × 1 for the geometrical optimization and 10 × 10 × 1 for the electronic-structure calculation at the equilibrium volume. The unit cell consists of five (001) crystal layers of GaP and a vacuum region between any two consecutive slabs equivalent to six layers. On top of the first layer we have added the sulfur adatoms. The bottom two layers of the slab were fixed at the ideal positions for simulating a bulk-like termination, while the three topmost layers of the slab and the S adatoms were given full freedom to move. To saturate the phosphorus (or gallium) dangling bonds on the back-side of the slab, the fictitious hydrogen atoms of charge 0.75 (1.25) were used. A planar dipole layer in the middle of the vacuum region as introduced by Neugebauer and Scheffler was also considered [19]. Throughout the calculations the calculated equilibrium lattice constant of 5.50 Å was used.

Results and discussions

Structural parameters

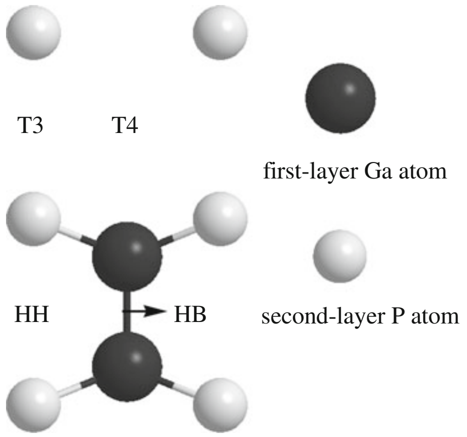

Fig. 1 Schematic plane view of the different adsorption sites for sulfur adsorption on the Ga-terminated GaP(001) (1 × 2) surface. HH, T3, HB, and T4 sites are labeled

When one sulfur atom was adsorbed on the Ga-terminated GaP(001) (1 × 2) surface, we took into account five possible adsorption sites, namely, HB, HH, T3, T4, and sub sites (see Fig. 1). They denote that the adatoms occupy the bridge, pedestal, valley bridge (on top of a third-layer atom), cave (on top of a fourth-layer atom) sites, and surface substitution site, respectively. The adsorption energies showed that the sulfur atom prefers to occupy the bridge site, consistent with the experimental results [3]. For the optimal bridge configuration, the S–Ga bond length is calculated to be 2.23 Å, close to the sum of covalent radii. The Ga–S–Ga bond angle is 98°, and the interplanar distance between the S and Ga atomic layer is 1.46 Å. The underlying Ga dimer becomes completely symmetric and the bond length is found to be 3.36 Å which is larger than that of clean surface (2.63 Å) (Table 1).

For 0.5 ML S adsorption on the P-terminated GaP(001) (1 × 2) surface, we considered similar adsorption sites. It turns out that the most stable structure is substitutional adsorption. One of the two P atoms in the outmost layer is replaced by a sulfur atom. The bridge site is less stable and the adsorption energy is larger by 0.18 eV. This result is

Table 1 Adsorption energy for 0.5 ML S adsorption on P- and Ga-terminated GaP(001) surfaces

	P-terminated surface					
Site	HB	T4	HH	T3	Sub	Subsurface
E_{ads}	−3.83	−3.75	−2.46	−2.07	−4.05	–
	Ga-terminated surface					
Site	HB	T4	HH	T3	Sub	Subsurface
E_{ads}	−4.59	–	−3.17	–	−3.45	−3.76

E_{ads} refers to the adsorption energy. It is defined by the formula $E = [E_{S/GaP(001)} - E_{GaP(001)} - NE_S]/N$, where $E_{GaP(001)}$ and $E_{S/GaP(001)}$ are the total energies of a clean GaP(001) surface and the adsorbate system, respectively, N is the number of sulfur atoms, and E_S is the total energy of a spin-polarized free sulfur atom similar to Se adsorption on GaAs(001) (1 × 2) system [20]. Furthermore, in the case of 0.5 ML S adsorption on the As-terminated GaAs(001) (1 × 2) surface, the electronic character for the substitutional adsorption geometry is in agreement with photoelectron core-level spectroscopy experiments [21]. For the substitutional adsorption configuration, we found that the bond length between P and S in the mixed dimer is about 2.25 Å while the S atom is 0.20 Å closer to the bulk than the P atom. The angle between the S–P bond and the second-layer Ga plane is about 72.5°, and the angle between the P–Ga bond and the second-layer Ga plane is about 77.0°. The vertical separation between the mixed dimer of S and P atoms can not be only explained from the difference of their covalent radii (0.04 Å), but can be explained by considering the difference in the ionic radii (0.28 Å). It also reveals the considerable charge transfer from P to S.

Recently, Tian et al. [11] found that a (2 × 2) reconstruction with rows of S–P and P–S pairs is the most stable structure in the case of 0.5 ML S adsorption on the P-terminated InP(001) surface. We also considered the similar geometry for 0.5 ML S adsorption on the P-terminated GaP(001) (2 × 2) surface. The optimal structure showed that the bond length of S–P dimer is 2.23 Å and the P atoms on the top surface are 0.21 Å above the plane of the two sulfur atoms, which is close to those for the case of 0.5 ML S adsorption on InP(001) (2 × 2) surface (2.23 and 0.24 Å) [11]. Its adsorption energy is found to be 0.11 eV smaller than that for 0.5 ML S adsorption on the P-terminated InP(001) (1 × 2) surface at substitution site. Nevertheless, compared with the 0.5 ML S adsorption on the Ga-terminated GaP(001) (1 × 2) surface at the bridge site, the structure of S-adsorbed P-terminated GaP(001) (2 × 2) surface is still 0.34 eV less stable. Therefore, we can conclude that the most stable structure is S-adsorbed Ga-terminated GaP(001) (1 × 2) surface at the bridge site for the case of 0.5 ML S adsorption on the GaP(001) surface, which agrees well with the experiments [3].

Electronic properties

Based on the optimized structures, we also investigated electronic properties for the representative configurations. Figure 2a shows the density of states (DOS) of the P-terminated GaP(001) (1 × 2) surface adsorbed with 0.5 ML S in energy-optimized substitution configuration. It turns out that the energy gap becomes larger by 0.37 eV than that of the clean surface (0.96 eV). It is expected that our calculated band gap is smaller than experimental measurement, since DFT method generally systematically underestimates the experimental results by about 30–40% the band gap in insulators and semiconductors [22] because the excited states of the electrons are not generated correctly. From the Fig. 2a, we also see that the DOS at E_f is vanished, which can be explained by the electron-counting argument. Each 1 × 2 unit cell with one P dimer has one electron deficient, i.e., each surface P atom needs 0.5 electron to completely fill the lone-pair state. The substitution of one P atom by S atom leads to 0.5 excess electrons since the S atom has one more electron than the P atom. This 0.5 electron exactly compensates for the other P atom in the unit cell. Thus, the dangling bond of this surface was all filled and the semiconductor character was stronger. The electronic band structure of this structure is also presented in Fig. 2b. The surface conduction band is mainly derived from the upper D2 subband, corresponding to the tip peak around 1.5 eV in Fig. 2a. The splitting of the two D1 subbands is mostly due to the different ionic potentials of S and P, and they are dispersionless.

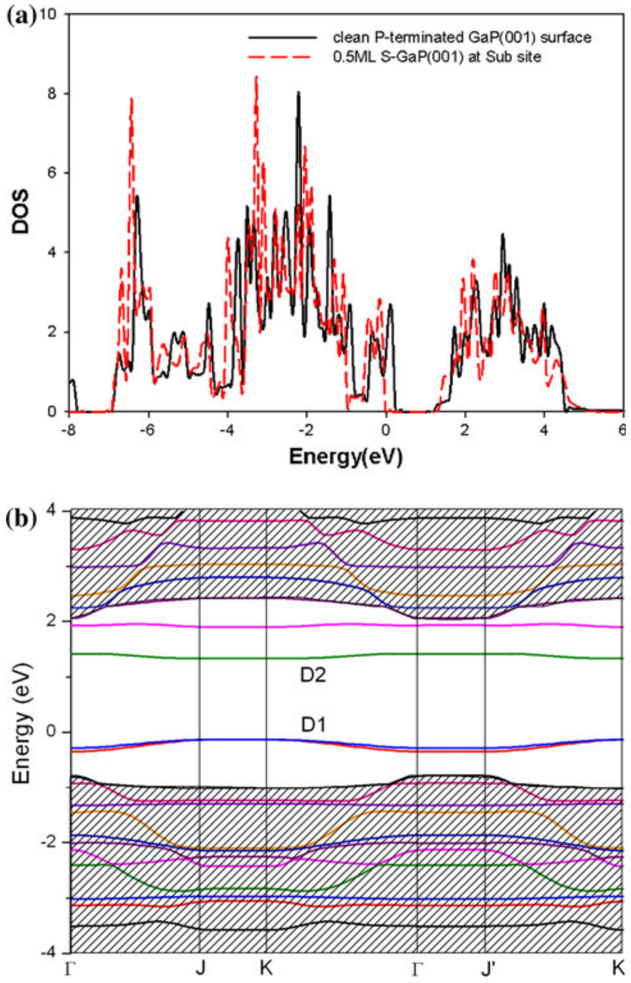

Fig. 2 Electronic structure of the P-terminated GaP(001) (1 × 2) surface with 0.5 ML S adsorption at the substitution site. **a** the total density of states **b** electronic band structure

The DOS of the Ga-terminated GaP(001) (1 × 2) surface adsorbed with 0.5 ML S in energy-optimized bridge configuration is presented in Fig. 3a. The surface state around the Fermi energy for the sulfur-adsorbated surface

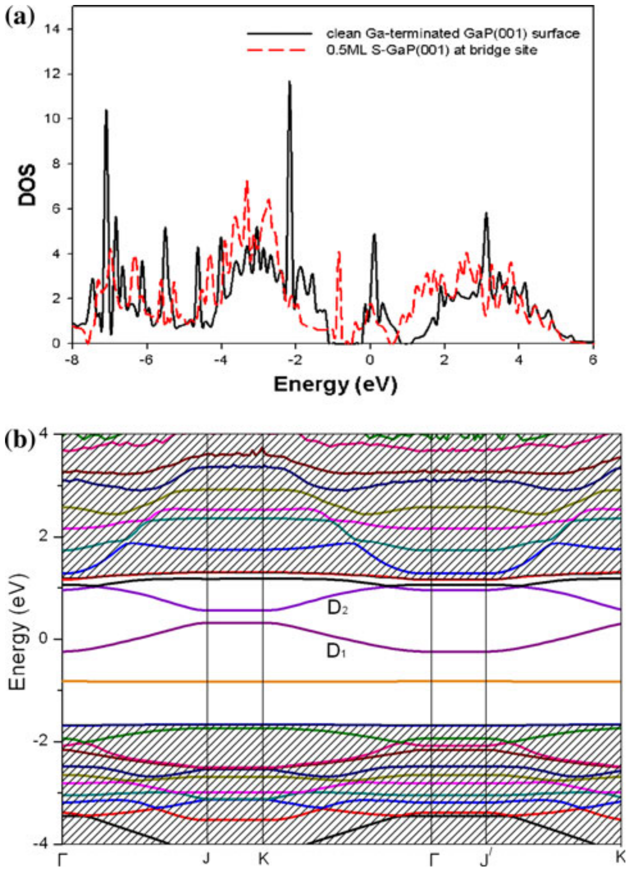

Fig. 3 Electronic structure of the Ga-terminated GaP(001) (1 × 2) surface with 0.5 ML S adsorption at the bridge site. **a** The total density of states **b** electronic band structure

was tremendously lowered relative to that for the clean surface, but not completely diminished. The result is in good agreement with the experiments by STM and IPES technique [2, 4]. The remained surface state at E_f did not include the contribution of S atoms, and it is composed of Ga-*p*, -*s*, and P-*p* orbitals. The corresponding electronic band structure is given in Fig. 3b.

We have also studied the S-induced work-function change, $\Delta\Phi$, of the GaP(001) (1 × 2) phase, which is defined as $\Delta\Phi = \Phi_{\text{S-substrate}} - \Phi_{\text{substrate}}$, where $\Phi_{\text{S-substrate}}$ and $\Phi_{\text{substrate}}$ are the work function of the system with and without S adsorbate, respectively. The changes of work-function due to S adsorption are found to be 1.44 and 0.45 eV for the Ga- and P-terminated surfaces, respectively, suggesting that some charge is transferred from the substrate to the S adsorbate.

Vibrational frequency of the 0.5 ML S adsorption on the GaP(001) surface

On the basis of the optimized geometries of the S-adsorbed Ga-terminated GaP(001) (1 × 2) surface at the bridge site, the vibrational properties were also estimated. This study was based on rigid substrate approximation, in which the slab was fixed at the optimized geometry of the considered chemisorption structure and the only dynamic atoms in the calculational unit cell are the sulfur atoms. The vibrational frequencies were calculated within the harmonic approximation, while the force constants were calculated with the central differential method. For the S-adsorbed Ga-terminated GaP(001) (1 × 2) structure, the vibrational frequencies of 32.37, 9.17, and 37.61 meV can be assigned to asymmetric (parallel), asymmetric, and symmetric (perpendicular) stretching modes, respectively. The Ga–S stretching vibrational frequency of 37.61 meV is comparable to the experimental value of 33.8–46.9 meV for metal-S stretching vibration [23].

Summary

The DFT–GGA method has been used to study the structural and electronic properties of the Ga- and P-terminated GaP(001) (1 × 2) surfaces adsorbed with 0.5 ML sulfur. For the S adsorption on the Ga- and P-terminated GaP(001) (1 × 2) surfaces, the sulfur atoms prefer to occupy the bridge sites and substitution sites, respectively. The case of 0.5 ML S adsorption on the P-terminated GaP(001) (2 × 2) surface with rows of S–P and P–S pairs was also considered. It was found that this structure is more stable than the configuration of S-adsorbed P-terminated GaP(001) (1 × 2) surface at the substitution site, but its adsorption energy is much larger than that for S-adsorbed Ga-terminated GaP(001) (1 × 2) surface at the bridge site. Therefore, we may conclude that the adsorption of sulfur on the Ga-terminated surface at the bridge site is the most stable structure for 0.5 ML S adsorption on the GaP(001) surface, agreeing well with the experimental results. The detailed structural parameters were also presented. Our analysis of electronic properties showed that the surface state around the Fermi energy is vanished for the case of S-adsorbed P-terminated GaP(001) (1 × 2) surface at the substitution site. For the configuration of S-adsorbed Ga-terminated surface at the bridge site, the surface state at E_f is tremendously lowered but not completely diminished, consistent with the experiments. The S-induced work-function changes on the Ga- and P-terminated surfaces are 1.44 and 0.45 eV, respectively, suggesting that some charge is transferred from the substrate to the S adsorbate. The calculated Ga–S stretching vibrational frequency of 37.61 meV is comparable to the experimental results.

Acknowledgements The authors acknowledge the Special Funds of the National Natural Science Foundation of China (Grant No. 10947102), Foundation of Education Committees of Chongqing (No.

KJ090503), Doctoral Foundation of Chongqing University of Posts and telecommunications (A2008-64).

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